

# Production of hydrogen by steam reforming of methanol on CeO<sub>2</sub> promoted Cu/Al<sub>2</sub>O<sub>3</sub> catalysts

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## Abstract

Catalytic production of hydrogen by steam reforming of methanol reaction has been developed on a series of co-precipitated Cu/Al<sub>2</sub>O<sub>3</sub> catalysts promoted with CeO<sub>2</sub> at atmospheric pressure in a microreactor. Effects of CeO<sub>2</sub> content, reaction temperature, methanol space velocity and H<sub>2</sub>O/CH<sub>3</sub>OH molar ratio on the catalytic activity have been investigated. CeO<sub>2</sub> promoted Cu/Al<sub>2</sub>O<sub>3</sub> catalysts exhibited higher activity and stability as compared to the unpromoted ones. The catalyst containing 20 wt.% of CeO<sub>2</sub> was the most active one with a methanol conversion of 95.5 mol%, H<sub>2</sub> selectivity of 99.9 mol% and the outlet CO concentration of 0.14 mol% at 250 °C. After 200 h of reaction, methanol conversion was still over 90.0% with the catalyst containing 20 wt.% of CeO<sub>2</sub>, while Cu/Al<sub>2</sub>O<sub>3</sub> catalyst deactivated rapidly after 100 h of reaction. Results of X-ray diffraction (XRD) and the surface element distribution of catalysts showed that CeO<sub>2</sub> not only greatly improved the surface copper dispersion and prevented copper crystallites from conglomeration or sintering, but also made copper crystallites relatively smaller. The improvement in activity and stability of the promoted catalysts was attributed to higher copper dispersion and smaller copper crystallites, and the synergetic effect of ceria.

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## 1. Introduction

Fuel cell powered electric vehicles and power plants using hydrogen as fuel are currently being developed in an effort to protect the environment and sustainable development [1,2]. Hydrogen produced by steam reforming of methanol is an increasing worldwide interest, the equilibrium conversion of steam reforming of methanol reaction reaches around 100% at 150 °C at atmospheric pressure [3]. Unfortunately, a considerable amount of CO (>100 ppm) as a by-product is produced during the reaction. As for the application of PEFC, even traces of CO (>20 ppm) in

the reformed gases deteriorate a Pt electrode and the cell performance is worsened [4]. An ideal method to produce hydrogen with lower amount of CO from steam reforming of methanol greatly requires a high performance catalyst, which must be highly active and selective for hydrogen production and also stable for a long period in a continuous operation. Now the most widely used catalysts for this reaction are copper containing catalysts since copper has been found to be high activity and selectivity for hydrogen production [5–9]. Copper containing catalysts are used in many catalytic reactions, such as CO shift at low temperature [10] and CO hydrogenation for methanol [11], steam reforming of methanol reaction gives copper containing catalysts new application.

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Furthermore, the high oxygen mobility, strong interaction with certain metals and the modifying ability make CeO<sub>2</sub> to be a very interesting promoter for catalysts [12–14], CeO<sub>2</sub> promoted catalysts have been rapidly developed in recent years [15].

The objective of the present investigation is to develop an efficient catalytic system based on CeO<sub>2</sub> promoted Cu/Al<sub>2</sub>O<sub>3</sub> catalysts by co-precipitation method for production of hydrogen by steam reforming of methanol reaction. The effects of catalyst composition, reaction temperature, methanol space velocity, H<sub>2</sub>O/CH<sub>3</sub>OH molar ratio on the performance of Cu/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, and the analysis of the surface element distribution and crystal phases and crystallite sizes of catalysts will be reported.

## 2. Experimental

### 2.1. Catalyst preparation

CeO<sub>2</sub> promoted Cu/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by co-precipitation method. A mixed aqueous solution of copper nitrate 3-hydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), aluminum nitrate 9-hydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and cerium nitrate 6-hydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), and a solution of sodium carbonate were added slowly and simultaneously into 100 ml of deionized water at 60 °C with vigorous stirring. The pH was kept constant at 7.0–7.2. The precipitates were aged at 60 °C for 30 min with vigorous stirring, then filtered and thoroughly washed with warm deionized water. The precipitates were dried overnight in air at 110 °C and calcined in a muffle oven at 500 °C for 3 h. Each calcined catalyst was pelletized in a hydraulic press, crushed, and sieved into a particle size of 0.45–0.55 mm, and used as catalysts for steam reforming of methanol reaction.

### 2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of catalyst samples were obtained using a Rigaku D/Max-3B with Cu K $\alpha$  radiation, a scanning angle ( $2\theta$ ) range of 10–80°, a scanning speed of 6° min<sup>-1</sup>, and a voltage and current of 35 kV and 30 mA, respectively, for the analysis of crystal phases and crystallite sizes. Crystallite sizes of Cu were calculated using Debye–Scherrer equation:  $t = 0.9\lambda/\beta \cos \theta$ , where  $\lambda$  is the wavelength

of radiation (1.5418 Å),  $\beta$  is the line broadening of the peak due to small crystallites (rad  $2\theta$ ), and  $\theta$  is the corresponding angle of the diffraction peak. The full width at half maximum (FWHM) of (1 1 1) reflection of copper was measured for calculating crystallite sizes [16]. The instrumental broadening was corrected by  $\beta = (B^2 - b^2)^{0.5}$ , where  $B$  is the total broadening, and  $b$  is the instrumental broadening. The surface element distribution of catalysts was analyzed with a PHI-5000C ESCA system (Perkin-Elmer) with Al K $\alpha$  radiation.

### 2.3. Activity measurements

Catalytic activity test experiments were made in a continuous flow fixed-bed microreactor (6 mm i.d.) placed in an electric furnace. The furnace temperature was controlled by a PID temperature controller with a K-type thermocouple inserted in the furnace. A separate thermocouple was used to monitor the temperature of the catalyst bed. This arrangement was capable of ensuring a temperature accuracy of  $\pm 1$  °C for the catalyst bed. All tests were conducted in a reaction temperature range of 180–280 °C at atmospheric pressure with 500 mg of the catalyst loaded in the reactor. The catalysts were reduced in situ with a premixed H<sub>2</sub>/Ar (5/95 (v/v)) gas flow, which had a speed of 80 ml min<sup>-1</sup> and was heated from room temperature to 300 °C at a rate of 1 °C min<sup>-1</sup>, and kept at 300 °C for 3 h. A typical test experiment for methanol steam reforming reaction at a methanol space velocity of 3.28 h<sup>-1</sup> with a 1:1 molar mixture of methanol and water was made as follows. The catalyst was loaded into the reactor and activated using designated activation procedure. The premixed water and methanol was then pumped to the vaporizer maintained at about 240 °C. The vaporized feed entered the reactor with a stream of Ar gas, which had a speed of 50 ml min<sup>-1</sup>, and then began the steam reforming reaction at the designated reaction temperature. The reaction products were analyzed on-line by HP5890 gas chromatography with thermal conductivity detector. The GC equipped with a 3 m long Porapak-Q column and a 3 m long Porapak-R column was able to detect both the liquid products, such as water, methanol, formaldehyde, methyl formate and dimethyl ether, and the gaseous products, such as H<sub>2</sub>, CO<sub>2</sub>, and CO, respectively. The catalytic activity was evaluated from the data recorded between

2 and 4 h of the continuous operation. In order to check the stability of catalysts, the reaction was also performed for a period of 100–200 h of the continuous operation at 250 °C. Blank run conducted with an empty reactor in a temperature range of 180–280 °C did not show any detectable methanol conversion.

### 3. Results and discussion

#### 3.1. Characterization of calcined catalysts

XRD patterns of Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> calcined catalysts are shown in Fig. 1, and XRD patterns of both catalysts after reaction are shown in Fig. 2. Fig. 1 shows that no alumina and ceria phases are detected, implying that aluminum and ceria phases are probably present in an amorphous-like or micro-crystallite state in catalysts, copper is present in a

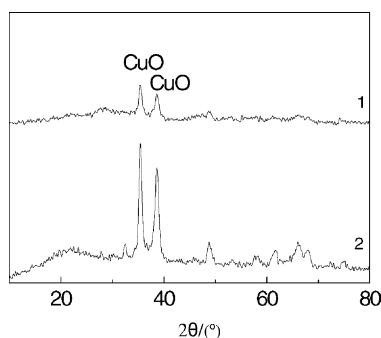


Fig. 1. XRD patterns of calcined catalysts (1)  $w(\text{CeO}_2) = 20\%$ ; (2)  $w(\text{CeO}_2) = 0\%$ .

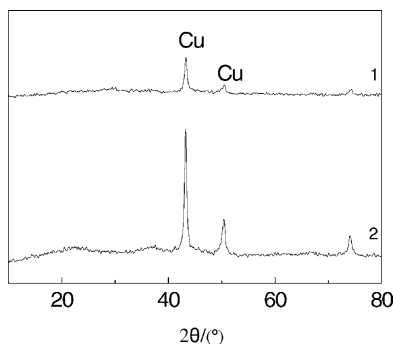


Fig. 2. XRD patterns of catalysts after reaction (1)  $w(\text{CeO}_2) = 20\%$ ; (2)  $w(\text{CeO}_2) = 0\%$ .

crystal state. The diffraction peak of copper is lowered remarkably for the catalyst containing 20 wt.% of CeO<sub>2</sub>, the higher the CeO<sub>2</sub> concentration, the lower the diffraction peak shows. In contrast to the catalyst containing 20 wt.% of CeO<sub>2</sub>, the diffraction peak of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst shows relatively sharp. It indicated that CeO<sub>2</sub> greatly promoted surface copper dispersion. Fig. 2 shows that only Cu diffraction peak is present after reaction. It indicated that Cu was the main activation center of catalysts. The crystallite sizes of copper ( $D_{\text{Cu}}$ ) are estimated from the half width of (1 1 1) reflection of Cu by Debye–Scherrer equation. The calculation results ( $D_{\text{Cu}}$  lowered from 23.9 to 19.8 nm) showed that copper crystallite sizes lowered with the addition of CeO<sub>2</sub>. XRD results showed that CeO<sub>2</sub> had a significant influence on surface copper dispersion and crystallite sizes.

The methanol decomposition and reforming reaction can be considered as the reverse of the methanol synthesis reaction using CO/H<sub>2</sub> or CO<sub>2</sub>/H<sub>2</sub> as a feed on copper containing catalysts [17]. For copper containing catalysts, Cu is the active site of methanol synthesis from CO<sub>2</sub> hydrogenation [18,19], so the dispersity and the surface element distribution of Cu acting specie are the factors determining the performance of catalysts. Table 1 shows the surface element distribution of catalysts. Copper content is 19.83 mol% and Cu/Al atom ratio is 0.25 on the surface of fresh Cu/Al<sub>2</sub>O<sub>3</sub> catalyst as compared with 24.83 mol% and 0.37 on the surface of fresh catalyst containing 20 wt.% of CeO<sub>2</sub>. After 100 h of reaction, copper content on the surface of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst is 17.26 mol% and Cu/Al atom ratio is 0.20, however, on the surface of the catalyst containing 20 wt.% of CeO<sub>2</sub>, even after 200 h of reaction, copper content is

Table 1  
The surface element distribution of catalysts

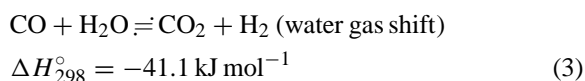
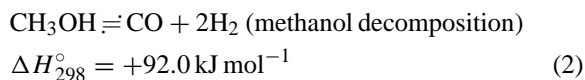
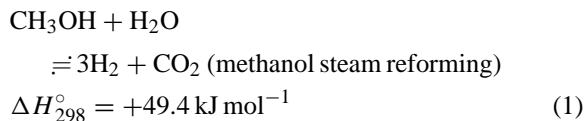
Catalysts		Cu (mol%)	Al (mol%)	Cu/Al (atom ratio)
Cu/Al <sub>2</sub> O <sub>3</sub>	Fresh	19.83	80.17	0.25
	After 100 h reaction	17.26	82.74	0.20
Cu/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Fresh	24.83	66.73	0.37
	After 200 h reaction	19.93	71.61	0.28

19.93 mol% and Cu/Al atom ratio is 0.28. It indicated that surface copper dispersion was much improved by CeO<sub>2</sub>, which would improve the catalytic performance. It can also be seen that Al content increases from 66.73 to 71.61 mol% on the surface of the catalyst containing 20 wt.% of CeO<sub>2</sub> as compared with that from 80.17 to 82.74 mol% on the surface of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. A higher Al content is favorable for the stabilization of copper structure on the catalyst surface. A XPS study [9,20] of Cu/Al-based catalysts showed that catalysts with higher copper dispersion might have exhibit Cu/Al interactions on their surfaces of calcined samples. The presence of Al would contribute the dispersion of oxidized copper species to a significant extent on the surface of calcined samples due to the formation of certain surface phases between Cu and Al, and the stabilization of isolated Cu species. During the subsequent reduction, these highly dispersed cations might behave as basic points for the formation of Cu particles with a higher surface area, consequently, which would have a significant influence on the catalytic performance.

### 3.2. Catalytic activity

Catalytic activity was evaluated in terms of methanol conversion (mol%). Methanol steam reforming reaction on CeO<sub>2</sub> promoted Cu/Al<sub>2</sub>O<sub>3</sub> catalysts in a wide temperature range showed that it was still active at a temperature as low as 180 °C. Analysis of the effluent gas indicated that H<sub>2</sub> and CO<sub>2</sub> were major components with a minor amount of CO. Other products such as formaldehyde, formic acid, methyl formate and dimethyl ether formed during reactions of methanol on Cu-based catalysts could not be detected under the reaction conditions [9,21].

Thus, the main reactions of the proposed route may be represented by Eqs. (1)–(3).



A systematic experiment was then undertaken after reducing the catalyst.

#### 3.2.1. Effect of CeO<sub>2</sub> concentration

Table 2 shows a typical dependence of methanol conversion on CeO<sub>2</sub> concentration in catalysts. An increase in methanol conversion with increasing CeO<sub>2</sub> concentration can be seen. Beyond 20.0 wt.% of CeO<sub>2</sub>, methanol conversion begins to decrease. The promoted catalysts display high selectivity for hydrogen and low selectivity for CO. It can also be seen that the outlet CO concentration is less than 0.2 mol%. Results showed that the promoted Cu/Al<sub>2</sub>O<sub>3</sub> catalysts exhibited better catalytic performance as compared to the unpromoted ones, it indicated that CeO<sub>2</sub> had an important influence on improving catalytic activity and decreasing the outlet CO concentration. Rosynek [22] considered that CeO<sub>2</sub> could oxidize hydrocarbon by itself. Although the catalytic activity of CeO<sub>2</sub> is lower than that of the oxides of other transition metals, the catalytic activity of Cu/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is greatly improved

Table 2  
Effect of CeO<sub>2</sub> concentration on catalytic activity

Number	w(CeO <sub>2</sub> ) (%)	X(CH <sub>3</sub> OH) (mol%)	Y(H <sub>2</sub> ) (mol (h·g) <sup>-1</sup> )	S(H <sub>2</sub> ) (%)	y(CO) (mol%)
1	0	81.4	0.2509	99.7	0.37
2	5	87.5	0.2697	99.9	0.19
3	10	90.0	0.2774	99.9	0.17
4	15	93.0	0.2866	99.9	0.15
5	20	95.5	0.2944	99.9	0.14
6	25	91.8	0.2829	99.9	0.16

Reaction conditions:  $P = 0.1 \text{ MPa}$ ;  $t = 250 \text{ }^{\circ}\text{C}$ ;  $X$  the methanol conversion;  $Y$  the hydrogen yield;  $S$  the selectivity; and  $y$  is the outlet CO concentration.

by the synergetic effect of ceria. Furthermore,  $\text{CeO}_2$  can improve the water gas shift reaction and promote CO conversion by this reaction, thus hydrogen with lower amount of CO can be produced on the promoted catalysts. On the other hand, results of XRD and the surface element distribution of catalysts showed that  $\text{CeO}_2$  promoted catalysts had high copper dispersion and small crystallite sizes. The improvement in the catalytic performance of the promoted catalysts was partly attributed to such a copper dispersion and crystallites. Table 2 shows that there is an optimum  $\text{CeO}_2$  concentration in the promoted catalysts. Such a maximum occurred for methanol conversion and  $\text{CeO}_2$  concentration is explained as below. An increase in  $\text{CeO}_2$  concentration means a decrease in the overall copper concentration in catalysts, consequently, a decrease in amounts of  $\text{Cu}^0$  in activated catalysts. The overall effect is the existence of a maximum ratio, inferring that, beyond the concentration limit for  $\text{CeO}_2$ , its synergetic effect begins decreasing while its role as an active site for methanol steam reforming reaction becomes significant. In comparison with copper species,  $\text{CeO}_2$  is less active if used solely as a catalyst [22].

### 3.2.2. Effect of reaction temperature

The effect of reaction temperature on catalytic performance of  $\text{CeO}_2$  promoted catalysts is shown in Fig. 3. Methanol conversion and hydrogen yield increase with increasing reaction temperature, while methanol is converted almost completely into  $\text{H}_2$ ,  $\text{CO}_2$ , and CO up to  $280^\circ\text{C}$ . In the temperature range of  $180$ – $280^\circ\text{C}$ , hydrogen selectivity remains almost unchanged, and the outlet CO concentration is less than  $0.4$  mol%. On the other hand, the outlet CO

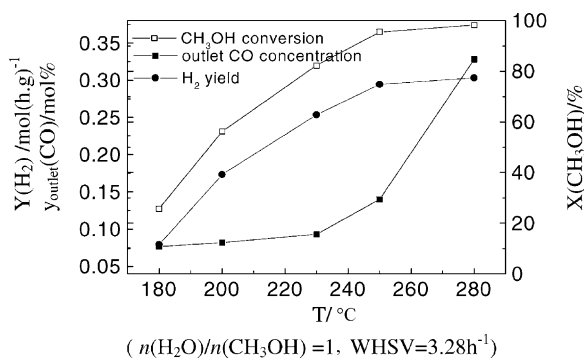


Fig. 3. Effect of reaction temperature on catalytic activity.

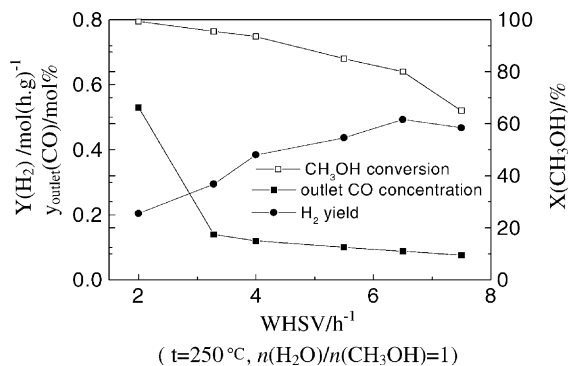


Fig. 4. Effect of WHSV on catalytic activity.

concentration increases with increasing reaction temperature. It indicates that CO is produced by the reverse reaction (Eq. (3)) at a higher temperature. Because the water gas shift reaction is exothermic, the increase in reaction temperature is not favorable for it.

### 3.2.3. Effect of methanol space velocity

Fig. 4 shows the effect of methanol space velocity (WHSV) on the catalytic performance of  $\text{CeO}_2$  promoted catalysts. Methanol conversion and the outlet CO concentration decrease with increasing methanol space velocity, and hydrogen yield has a maximum in the experiment conditions. On the other hand, methanol space velocity does not affect the selectivity of  $\text{H}_2$ , which remains around 99.9% throughout the experiment. In the present study, a methanol space velocity of  $3.28 \text{ h}^{-1}$  has been chosen for the evaluation of the performance of catalysts during the steam reforming reaction.

### 3.2.4. Effect of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ molar ratio

It is known from Eqs. (1)–(3) that excess  $\text{H}_2\text{O}$  promotes methanol conversion and reduces CO concentration by shifting the equilibrium (Eq. (3)) toward the right. The effect of  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio on the catalytic performance during the steam reforming of methanol reaction at  $250^\circ\text{C}$  is presented in Fig. 5. It can be seen that methanol conversion increases remarkably with increasing the  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio below 1.0, while the increase slows down beyond the ratio of 1.0, and hydrogen yield increases slowly with increasing  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio. An outlet CO concentration of  $0.78$  mol% is determined

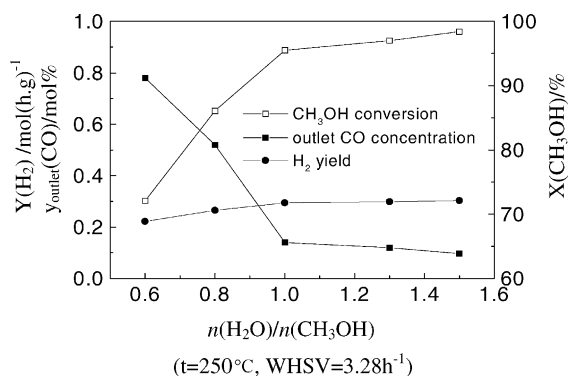


Fig. 5. Effect of  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio on catalytic activity.

when the  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio is 0.6. It should be noted from Fig. 5 that the outlet CO concentration decreases to about 0.1 mol% with increasing the  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio up to 1.5. Hence, the results showed that higher  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio was favorable for reducing the outlet CO concentration due to the enhancement of WGS reaction. Therefore, an  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio between 1.0 and 1.5 offered a better catalytic performance in the present experimental conditions.

### 3.2.5. Effect of reaction time

In order to investigate the stability of catalysts during the steam reforming reaction, the continuous operations were performed at  $250^\circ\text{C}$  and 0.1 MPa with catalysts containing 0 wt.% of  $\text{CeO}_2$  and 20 wt.% of  $\text{CeO}_2$  for a period of 100–200 h, and the results are shown in Fig. 6. It can be seen that  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst

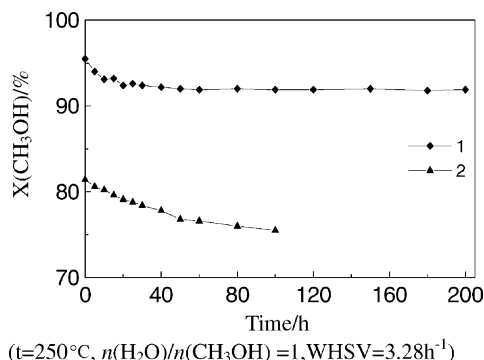


Fig. 6. Effect of reaction time on catalytic activity (1)  $w(\text{CeO}_2) = 20\%$ ; (2)  $w(\text{CeO}_2) = 0\%$ .

deactivates rapidly after 100 h and methanol conversion decreases from 81.4 to 75.8%, approximately a decrease of 6.87%. There is an initial deactivation of the catalyst containing 20 wt.% of  $\text{CeO}_2$  before 20 h of continuous operation. After 20 h of that, no significant deactivation of the catalyst is observed even after 200 h, and methanol conversion remains almost unchanged throughout this period. As far as the product selectivity is concerned, there is no change in the selectivity of  $\text{H}_2$ , which is around 99.9 mol%. The result showed that  $\text{CeO}_2$  improved the stability of catalysts.

## 4. Conclusions

The addition of  $\text{CeO}_2$  to  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst increases its activity and stability for hydrogen production from methanol steam reforming. Methanol conversion increases with increasing  $\text{CeO}_2$  concentration below 20 wt.%. Increase in reaction temperature and  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  molar ratio also improves methanol conversion. On the other hand, methanol conversion decreases with increasing methanol space velocity. Hydrogen selectivity remains unchanged in the experimental conditions, the outlet CO concentration is less than 0.8 mol%. Results of XRD and the surface element distribution of catalysts showed that  $\text{CeO}_2$  could enhance the surface dispersion of copper on catalysts, and prevent copper crystallites from sintering or conglomerating, and make copper crystallites relatively smaller. It is suggested that high activity, selectivity and stability of  $\text{CeO}_2$  promoted catalysts have been resulted from a higher copper dispersion and smaller copper crystallites, and the synergetic effect of ceria.

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